UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF CHEMICAL SAFETY
AND POLLUTION PREVENTION

OFFICE OF PESTICIDE PROGRAMS
REGISTRATION DIVISION (7505P)

December 6, 2018

**MEMORANDUM:**

| | | |
|---|---|---|
| Subject: | Name of Pesticide Product: | CAPTAIN LIQUID COPPER ALGAECIDE |
| | EPA Reg. No. /File Symbol: | 67690-9 |
| | DP Barcode: | DP 449996 |
| | Decision No.: | 542817 |
| | Action Code: | R340 |
| | Submission: | #1022433 |
| | E-Submission: | 30817 |
| | PC Code: | 024409 (Copper ethanolamine complex: 28.2%) |

From: Byron T. Backus, Ph.D., Toxicologist
CITAB
Registration Division (7505P)

Through: Eugenia McAndrew, Biologist
CITAB
Registration Division (7505P)

To: Craig Reeves, PM 22
Fungicide Branch
Registration Division (7505P)

Registrant: SEPRO CORPORATION

FORMULATION FROM LABEL:

| Active Ingredients: | by wt. |
|---|---|
| 024409 Copper Ethanolamine Complex*……..…..……..……. | 28.2% |
| Other Ingredients:…….. | 71.8% |
| TOTAL | 100.0% |

*Metallic copper equivalent = 9.1%

**ACTION REQUESTED:** "…BEAN Acute Toxicology package includes the following:

2nd Bean: to consider and clarify toxicological categories, based on discussions of 11/27/2018 (FB, CITAB)…"

**BACKGROUND:** This is an application for pesticide amendment. The registrant is requesting a change in the signal word from DANGER to WARNING, with additional revisions in precautionary labeling. The proposed label indicates that this product would be in toxicity category II for eye irritation and toxicity category III for dermal irritation. In a previous CITAB review (November 1, 2018) for 67690-9, this formulation was assigned to Toxicity Category II for eye irritation and dermal irritation, with a revision in the signal word from DANGER to WARNING.

**COMMENTS AND RECOMMENDATIONS**:

1. According to the data matrix dated 16 July 2018 the registrant is citing MRID 50621202 for eye irritation and 50621201 for dermal irritation. However, MRID 40864102 (which contains oral $LD_{50}$, dermal $LD_{50}$, eye irritation and dermal irritation studies) has previously been cited for this and similar products.

2. In the eye irritation study (pages 45-52 of MRID 40864102) 6 eyes were exposed. At 72 hours 1/6 eyes was positive for corneal opacity and 5/6 (including the eye that was positive for corneal opacity) were positive for conjunctival effects. At 14 days all eyes were clear (indicating Toxicity Category II for eye irritation). The report does not indicate the composition of the test material in these studies (other than 9.1% active, consistent with the metallic copper equivalent for 67690-9) which were submitted for 12014-UR (never registered, withdrawn August 7, 1989). The following are the eye irritation scores on day 14:

OBSERVATION PERIOD: 14 days

| Animal No./ Ear Tag No. 6520- | 4236 | 4237 | 4238 | 4225 | 4240 | 4224 |
|---|---|---|---|---|---|---|
| Location of Corneal Lesions Tail <——> Head | ◯ | ◯ | ◯ | ◯ | ◯ | ◯ |
| Ocular Structure | | | | | | |
| Cornea - Opacity | 0 | 0 | 0 | 0 | 0 | 0 |
| Area | 0 | 0 | 0 | 0 | 0 | 0 |
| Iris | 0 | 0 | 0 | 0 | 0 | 0 |
| Conjunctivae - | | | | | | |
| Redness | 0 | 0 | 0 | 0 | 0 | 0 |
| Chemosis | 0 | 0 | 0 | 0 | 0 | 0 |
| Discharge | 0 | 0 | 0 | 0 | 0 | 0 |
| Sodium Fluorescein Exam | Neg | Neg | Neg | Neg | Neg | Neg |
| Technician | dw | dw | dw | dw | dw | dw |
| Recorded By | dw | dw | dw | dw | dw | dw |
| Date 1983 | 1/27 | 1/27 | 1/27 | 1/27 | 1/27 | 1/27 |

A = Purulent Discharge
B = Clear Discharge
C = Petite Hemorrhage
D = Blanching
INJ = Injected
NEG = Negative
POS = Positive

E = Corneal Epithelial Damage, Peeling
F = Corneal Epithelial Damage, Piling
G = Corneal Epithelial Damage, Pitting
H = Pannus
I = Corneal Neovascularization
NA = Not Applicable

A PRD memorandum (Gregg, October 18, 2010) for 67690-9 states that MRID 408641-02 was cited by the registrant to satisfy the eye and dermal irritation study requirements (81-4 and 81-5) and that: "…RMIB V concurs with the earlier PRB / SRRD review concerning the acceptability of the studies based on PRS / RD reviews…" The PRD memorandum of October 18, 2010 assigned 67690-9 to toxicity category I for eye irritation. Two previous PRD memoranda (M. Lewis, September 22, 2008 and M. Lewis, October 9, 2008) also indicated that EPA Reg. No. 67690-9 was in toxicity category I for eye irritation based on the study in MRID 40864102. Both PRD memos include the statement: "These studies were reviewed and found to be acceptable by PRS/RD on 8/10/91, 4/10/92, & 10/26/93. After reviewing the studies PRB concurred [concurs] with RD's findings."

3. The eye irritation study in MRID 50621202 has been previously reviewed (McAndrew, CITAB memorandum dated 18 September 2018 for 67690-81) and classified as acceptable. The results of this study indicated the test material (Captain, Lot #: 2018-17276, containing 28.2% copper ethanolamine complex; 71.8% other ingredients. pH = 10.0 to 10.5. Described as a blue liquid) is in Toxicity Category III for eye irritation.

4. As previously stated in the CITAB review of November 1, 2018 for 67690-9: "After taking into consideration the results of the eye irritation studies in MRIDs 40864102 (Toxicity Category II) and 50621202 (Toxicity Category III), CITAB concludes that an assignment of 67690-9 to Toxicity Category II for eye irritation is appropriate.

5. The dermal irritation study (dated December 19, 2016) in MRID 50333701 was conducted at Product Safety Laboratories; the test material was identified as the formulation for 67690-9. As stated in the CITAB memorandum dated November 1, 2018: "The test material was Captain, Lot # 2016-15031, a copper ethanolamine complex (CAS #82027-59-6 and 14215-52-2) – 28.2%; 71.8% other ingredients, a blue liquid, pH = 10.0 to 10.5. 0.5 mL was applied to a 6-$cm^2$ test site on each of 3 NZW rabbits, with 4-hr semi-occlusive exposure. Dose sites were scored (Draize) at 30-60 minutes and at 24 hours after patch removal. At 30-60 minutes 2 sites scored 1 for erythema and 1 for edema, while the third site scored 2 for erythema and 0 for edema; blue staining was noted at all 3 test sites. At 24 hours two sites scored 2 for erythema and 1 for edema; corrosion was noted at the third site with a score of 4 for erythema and 2 for edema. with corrosion noted. Due to corrosion at one dose site, the study was terminated following the 24-hour scoring." The results of this study indicate 67690-9 is in toxicity category I for dermal irritation.

6. The dermal irritation study in MRID 50621201 has been previously reviewed (McAndrew, CITAB memorandum dated 18 September 2018 for 67690-18) and classified it as acceptable. The results (At 48 and 72 hours 2/3 sites scored 1 and 1/3 scored zero for erythema. "Small areas of dark discoloration were noted at one dose site between 30-60 minutes through 72 hours. All scores were zero on Day 7. PDII = 1.17) indicate the test material (Captain, Lot #: 2017-16324. Copper ethanolamine complex (CAS #82027-59-6 and 14215-52-2) – 28.2%; 71.8% other ingredients, described as a blue liquid, pH = 10.0 to 10.5) is in Toxicity Category IV for dermal irritation.

7. The dermal irritation study in MRID 50333702 was reviewed in the CITAB memorandum of November 1, 2018 for 67690-9. The test material was Captain, Lot # 2017-15693, a copper ethanolamine complex (CAS #82027-59-6 and 14215-52-2) – 28.2%; 71.8% other ingredients, a blue liquid, pH = 10.0 to 10.5. 0.5 mL was applied to a 6-$cm^2$ test site on each of 3 NZW rabbits, with 4-hr semi-occlusive exposure. Dose sites were scored (Draize) at 30-60 minutes and at 24, 48 and 72 hours after patch removal. At 30-60 minutes 2 sites scored 1 for erythema and 1 for edema, while the third site scored 0 for both. At 24 hours one site scored 1 for both erythema and edema, while the other two sites scored zero for both. At 48 and 72 hours all scores were zero. The PDII = 0.5, indicating Toxicity Category IV.

8. From the results of the three dermal irritation studies in MRIDs 50333701 (Toxicity Category I), 50333702 (Toxicity Category IV), and 50621201 (Toxicity Category IV), CITAB has concluded that 67690-9 can be assigned to Toxicity Category II for dermal irritation. The study in MRID 50333701 states that there was blue staining at all dose sites at 30-60 minutes after patch removal (not mentioned in the other studies; in MRID 50621201 one site had "small areas of dark discoloration" which were still present at 72 hours).

   Previous PRB reviews for 67690-9 (M. Lewis, September 22, 2008, M. Lewis, October 9, 2008, and B. Gregg, October 18, 2010) assigned 67690-9 to Toxicity Category II for dermal irritation.

9. As stated in the CITAB review of November 1, 2018, the following is the revised acute toxicity profile for 67690-9:

| | | | |
|---|---|---|---|
| Acute oral $LD_{50}$ (rat) | Tox. Category III* | Cited | MRID 43063402 |
| Acute dermal $LD_{50}$ (rat) | Tox. Category III | Cited | MRID 42691801 |
| Acute inhalation $LC_{50}$ (rat) | Tox. Category III** | Cited | MRID 43847802 |
| Eye irritation (rabbit) | Tox. Category II | Acceptable | MRIDs 40864102 (II) |
| | | Acceptable | 50621202 (III) |
| Dermal irritation (rabbit) | Tox. Category II*** | Acceptable | MRIDs 50333701 (I) |
| | | Acceptable | 50333702 (IV) |
| | | Cited | 40621201 (IV) |
| Dermal sensitization (g. pig) | Non-sensitizer | Cited | MRID 43063403 |

*Acute oral $LD_{50}$ females = 580 mg/kg
**Acute inhalation $LC_{50}$ females = 2.0 mg/L
***Primary dermal irritation Mean Score = 4.9 at 72 hours with severe irritation noted

This product meets the requirements for Child Resistant Packaging if there are residential uses on the label.

10. Based on the acute toxicity profile given above, the following is the precautionary and first aid labeling for 67690-9, as obtained from the Label Review System:

**PRODUCT ID #:** 67690-9

**PRODUCT NAME:** Captain Liquid Copper Algaecide

**PRECAUTIONARY STATEMENTS**

**SIGNAL WORD:** WARNING

**SPANISH SIGNAL WORD:** AVISO
Si usted no entiende la etiqueta, busque a alguien para que se la explique a usted en detalle.
(If you do not understand the label, find someone to explain it to you in detail.)

**Hazards to Humans and Domestic Animals:**

Causes substantial but temporary eye injury. Causes skin irritation. Harmful if swallowed or absorbed through skin. Harmful if inhaled. Do not get in eyes, on skin or on clothing. Avoid breathing spray mist. Wash thoroughly with soap and water after handling and before eating, drinking, chewing gum, using tobacco or using the toilet. Remove and wash contaminated clothing before reuse.

Wear coveralls over short-sleeved shirt and short pants, socks, chemical resistant footwear and chemical resistant gloves (barrier laminate, butyl rubber, nitrile rubber, neoprene rubber, polyvinyl chloride or Viton). Wear appropriate protective eyewear (such as goggles, face shield or safety glasses).

When mixing and loading wear a chemical-resistant apron. For overhead exposure wear chemical-resistant headgear. When cleaning equipment wear a chemical-resistant apron.

**First Aid:**

If in eyes:
-Hold eye open and rinse slowly and gently with water for 15-20 minutes.
-Remove contact lenses, if present, after the first 5 minutes, then continue rinsing eye.
-Call a poison control center or doctor for treatment advice.

If on skin or clothing:
-Take off contaminated clothing.
-Rinse skin immediately with plenty of water for 15-20 minutes.
-Call a poison control center or doctor for treatment advice.

If swallowed:
-Call a poison control center or doctor immediately for treatment advice.
-Have person sip a glass of water if able to swallow.
-Do not induce vomiting unless told to do so by a poison control center or doctor.
-Do not give anything by mouth to an unconscious person.

If inhaled:
-Move the person to fresh air.
-If person is not breathing, call 911 or an ambulance, then give artificial respiration, preferably by mouth-to-mouth if possible.
-Call a poison control center or doctor for further treatment advice.

Have the product container or label with you when calling a poison control center or doctor or going for treatment. You may also contact 1-800-xxx-xxxx for emergency medical treatment information.

**User Safety Recommendations**:

Users should:
-Wash hands before eating, drinking, chewing gum, using tobacco or using the toilet.
-Remove clothing/PPE immediately if pesticide gets inside. Then wash thoroughly and put on clean clothing.
-Remove PPE immediately after handling this product. Wash the outside of gloves before removing. As soon as possible, wash thoroughly and change clothing.

**Notes**:

Since this product is no longer in Toxicity Category I for eye and/or dermal irritation, the statement "Probable mucosal damage may contraindicate the use of gastric lavage" is no longer needed.

This product meets the requirements for Child Resistant Packaging based on acute oral toxicity, acute inhalation toxicity and primary dermal irritation if there are residential application sites on the product label. Unless this product meets any of the exemptions per 40 CFR 157.24, Child Resistant Packaging is required.

*Based on information in the CSF, acceptable chemical-resistant **[not waterproof]** glove compositions would be Barrier Laminate, Butyl Rubber ≥ 14 mils, Nitrile Rubber ≥ 14 mils, Neoprene Rubber ≥ 14 mils, Polyvinyl Chloride (PVC) ≥ 14 mils, and Viton ≥ 14 mils.*

*The proposed label includes the statement under PERSONAL PROTECTIVE EQUIPMENT (PPE): "If you want more options, follow the instructions for category A on an EPA chemical-resistant category selection chart." This statement should be deleted (from page 10-9 of the current Label Review Manual: NOTE: The EPA Chemical Resistance Category Selection Chart for Gloves should never be placed or referenced on the product label; it is intended for EPA and registrant guidance only).*

**Reviewer:** Byron T. Backus, Ph.D.
**Date:** December 6, 2018
**Risk Manager (EPA):** 22

The following is the Acute Toxicity Data Evaluation Record (DER) for one of the eye irritation studies submitted or cited to support the revision in signal word (from DANGER to WARNING) for EPA Reg. No. 67690-9 (label declaration: Copper Ethanolamine Complex: 28.2% [Metallic copper equivalent = 9.1%]).

| | | | | |
|---|---|---|---|---|
| **1. DP BARCODE:** 448387 | | | | |
| **2. PC CODE:** 024409 (Copper ethanolamine complex: 28.2% [Metallic copper equivalent: 9.1%]) | | | | |
| **3. CURRENT DATE:** December 6, 2018 | | | | |
| **4. TEST MATERIAL:** 9.1% A&V PLUS, EPA File Symbol 12014-UR; pH = 9.49 | | | | |
| **Study** | **MRID** | **Results** | **Tox Cat** | **Core Grade** |
| Primary eye irritation / rabbit / Hazelton Laboratories, Wisconsin / Lab No. 732464 / Jan. 27, 1983 / OCSPP 870.2400; OECD 405 | 40864102 | 0.1 mL was instilled into the right eye of each of 6 rabbits, with no subsequent wash. **Results:** one rabbit vocalized following instillation. At one hour one eye showed grade 1 corneal opacity (area = 1); all eyes showed iritis and all eyes were positive for conjunctival irritation. 24 and 48 hours: one eye had grade 1 or 2 corneal opacity (area = 1), three eyes had grade 1 iritis, and all eyes were positive for conjunctival irritation. 72 hours: one eye had grade 1 corneal opacity (area = 1); one eye had iritis. Five eyes were positive for conjunctival irritation (all 5 had petite hemorrhage and blanching, and one also had areas of possible necrotic tissue). Day 7: none of the eyes had corneal opacity or iritis. One eye had grade 2 conjunctival redness with petite hemorrhage, blanching, and areas of possible necrotic tissue. One eye had grade 1 redness with petite hemorrhage. Day 14: all irritation had cleared (all scores were zero). | II | A |

**n.d. = not determined; Core Grade Key: A =Acceptable, S = Supplementary, W = Waived, U = Unacceptable, D = Data Gap**